

Low temperature anode-supported solid oxide fuel cells based on gadolinium doped ceria electrolytes[☆]

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Abstract

The utilization of anode-supported electrolytes is a useful strategy to increase the electrical properties of the solid oxide fuel cells, because it is possible to decrease considerably the thickness of the electrolytes. We have successfully prepared single-chamber fuel cells of gadolinium doped ceria electrolytes $\text{Ce}_{1-x}\text{Gd}_x\text{O}_{2-y}$ (CGO) supported on an anode formed by a cermet of NiO/CGO. Mixtures of precursor powders of NiO and gadolinium doped ceria with different particle sizes and compositions were analysed to obtain optimal bulk porous anodes to be used as anode-supported fuel cells. Doped ceria electrolytes were prepared by sol–gel related techniques. Then, ceria-based electrolytes were deposited by dip coating at different thicknesses (15–30 μm) using an ink prepared with nanometric powders of electrolytes dispersed in a liquid polymer. Cathodes of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ (LSCO) were also prepared by sol–gel related techniques and were deposited on the electrolyte thick films. Finally, electrical properties were determined in a single-chamber reactor where propane, as fuel, was mixed with synthetic air below the direct combustion limit. Stable density currents were obtained in these experimental conditions. Flux rate values of the carrier gas and propane partial pressure were determinants for the optimization of the electrical properties of the fuel cells.

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1. Introduction

In recent years, a new type of SOFC, the single-chamber fuel cell, which shows very high current density at low temperatures (450–630 °C), has been developed by different research groups [1–10]. The main difference between the one-chamber fuel cells and the conventional two-chamber fuel cells is that, in the former, both electrodes are simultaneously in contact with both the fuel and the air. The advantages of such SOFCs are that they do not need expensive materials, they are very simple to fabricate, and it is very easy to assemble them into multiple stacks. These SOFCs can work directly with hydrocarbons (internal reforming) because the temperature at which they operate is adequate for hydrocarbon reforming in the anode. Moreover, the poisoning of the Ni by carbon or sulphur is not possible due to the presence of air on the anode electrode.

Solid oxide electrolytes based on ceria doped materials are considered to be one of the most promising candidate materials for use in single-chamber, low temperature solid oxide fuel cells, because they offer considerably higher ionic conductivity than YSZ in the range of 450–700 °C. The substitution of Ce^{4+} by suitable trivalent cations such as Gd^{3+} , Sm^{3+} , Y^{3+} or La^{3+} enhances the chemical stability, increases the ionic conductivity and suppresses the reducibility of ceria-based materials. The most effective substitutes are Gd_2O_3 and Sm_2O_3 possibly due to the fact that they minimize the changes in lattice parameter.

Both, electrolyte- and anode-supported fuel cells have been reported for these doped ceria fuel cells based in one chamber reactor. However, there is some difficulty to find stable cathodes in one-chamber fuel cells under the proposed reducing conditions. Hibino et al. [8] reported a relatively high peak power density at 500 °C for an electrolyte-supported fuel cell using $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ mixed with $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (SSC + CSO) as the cathode and ethane as the fuel. However, they found that this cathode was incompatible with propane at temperatures higher than 450 °C. It should be noted that, because of the heat release during partial exothermic oxidation at the anode, the actual temperature of the fuel cell is higher than the furnace temperature,

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depending on the operation conditions [9]. This self-heating in single-chamber fuel cells explains the higher power densities obtained from single-chamber, as compared with dual-chamber, fuel cells at lower apparent furnace temperatures. Shao et al. have presented a new cathode ($\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$), which works well with propane as fuel in an anode-supported single-chamber fuel cell based on CSO electrolytes [10]. We show in the present work that the cathode $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (LSCO) is stable up to 640°C in an anode-supported single-chamber fuel cell with propane diluted in air as fuel. Moreover, we have found that fuel cells with LSCO as cathode are also stable with CSO as electrolyte, in the same operating conditions with propane as fuel.

Some authors have reported that ceria-gadolinia (CGO) possesses the highest values of ionic conductivity [11] and this was confirmed by computer atomistic simulations based on a combination of coulomb interactions and lattice relaxation [12]. This interaction is dependent on the size of the trivalent additive and the simulations suggest that the optimum radius for the trivalent cation in ceria-based oxide nearly corresponds to Gd^{3+} . Nevertheless, other authors have reported higher values of ionic conductivity for ceria-samarium (CSO) materials [13,14]. Some of the differences between results reported by different authors can also be related to differences in powder preparation and the corresponding effects on the relative role of the resistive grain boundary [15,16]. For this reason one may expect some improvements by optimizing the sample preparation method. It is thus far from clear whether the properties of CGO exceed those of CSO. In this work, we present the results with CGO, but we have found similar results for CSO.

2. Experimental

2.1. Powder preparation

Powder mixtures of 60–80% of NiO and 40–20% of CGO, respectively, for anode substrate fabrication and powders of LSCO for cathodes were prepared by the acrylamide sol-gel

related methods starting from nitrate solutions of the different cations. Cermets of NiO-CGO for anodes were prepared by coprecipitation and calcination in order to obtain homogeneous mixtures of both phases with very small grain size. All of these powders were characterized by XRD and the patterns showed no evidences of secondary phases. The powders for the $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ electrolytes were prepared by the sol-gel acetyl-acetonate method starting from acetates: $\text{Ce}(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot 1.5\text{H}_2\text{O}$ (Alfa Aesar, 99.9% purity) and $\text{Gd}(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot x\text{H}_2\text{O}$ (Alfa Aesar, 99.9% purity) as described elsewhere [16]. Finally, 2% by weight of $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_3$ was added in order to reduce the densification temperature of the thick film electrolyte deposited on the anode [17].

2.2. Anode and electrolyte preparation

Cylindrical pellets of NiO and CGO (80–20%, 70–30% and 60–40%, respectively) 10 mm of diameter and a thickness of ~ 0.5 mm were prepared by uniaxial pressing at 3 tonnes cm^{-2} during 30 s. Then, thick films of CGO were deposited by dip-coating on the green pellets, using an ink prepared from powders obtained by the acetyl-acetonate technique. Finally, the pellets were heated between 1350 and 1440°C during 5 h in order to ensure the anode consolidation and the electrolyte densification. The microstructural analysis of the sintered samples and measurement of the thickness of the CGO electrolytes were performed by scanning electron microscopy (SEM). A homogeneous phase distribution was found for the NiO/CGO anodes and a very high density for the CGO electrolyte films. Fig. 1 shows the variation of the grain size and porosity as a function of NiO-CGO composition for different cermets calcined at a constant temperature of 1350°C . We can see that porosity and grain size of NiO and CGO materials increase with NiO proportion. So, the greatest coarsening of NiO particles was observed for samples with 80% of NiO and 20% of CGO. Optimal fuel cell electrical properties were found for a ratio of NiO-CGO equal to 60–40%, respectively.

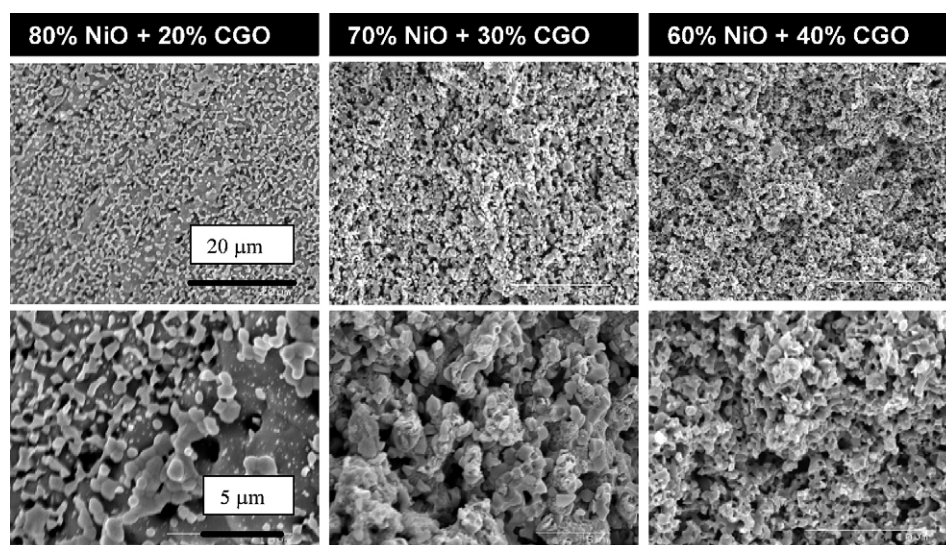


Fig. 1. SEM pictures of sintered anodes with different NiO-CGO composition prepared at 1350°C .

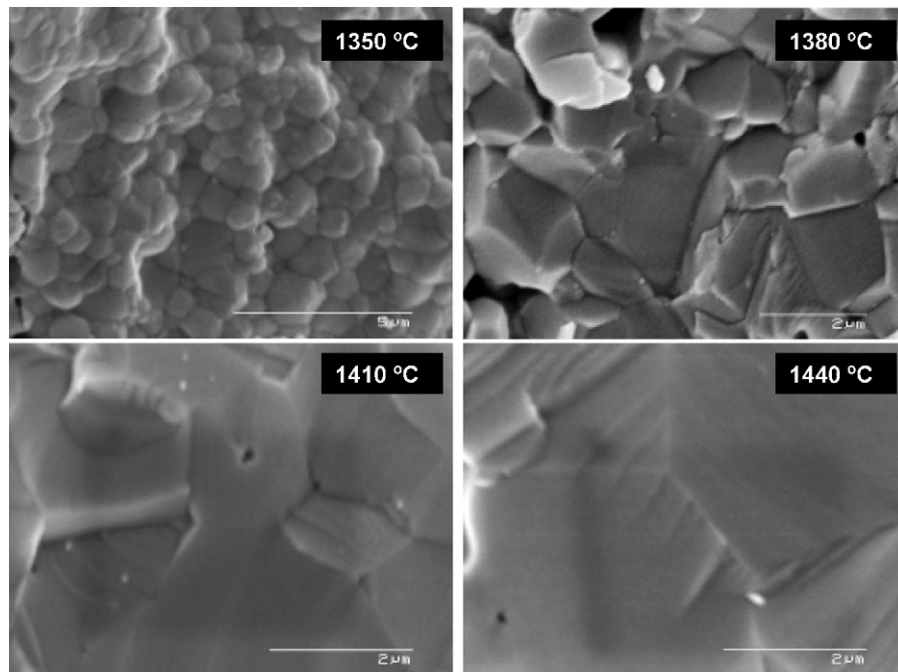


Fig. 2. SEM pictures of dense sintered electrolytes prepared at different temperatures.

Electrolyte densification takes place simultaneously during the anode consolidation in the same thermal treatment. Fig. 2 shows the variation of the CGO electrolyte grain size as a function of annealing temperature. We can see that the diameter of the CGO grains increases drastically from 1350 to 1440 °C, but the densification of the electrolyte is not observed at temperatures below 1340 °C. The pellets (anode + electrolyte) were annealed 5 h at 900 °C in Ar/H₂ 5% before the cathode deposition in order to obtain a cermet of Ni/CGO. The best electrical properties were found in samples prepared between 1350 and 1400 °C. Probably, because the ionic conductivity of the electrolyte increases when the grain size decreases, at similar densification [17].

2.3. Cathode preparation

Mixtures of LSCO+CGO 10% by weight were prepared from the powders obtained by the acrylamide sol–gel method. The powders were mixed in an agate mortar with a commercial resin and were deposited by dip-coating directly on the dense CGO electrolyte films. Finally, the fuel cells were annealed at 950 °C in an argon atmosphere. The same ink was used for electrical contacts on the cathode. Then, the resin was eliminated during heating in the reactor with the same atmosphere where the electrical measurements were made. In Fig. 3, we have represented in detail the structure of a complete anode-supported fuel cell with the anode and electrolyte annealed at 1350 °C (see Fig. 3a). In Fig. 3b, c and d we show the microstructure at bigger magnification of the electrolyte, anode and cathode, respectively. The thickness of the CGO electrolyte is ~15 μm and the grain size average is ~1 μm. The porosity in the cathode looks bigger than in the anode because the temperature of the last thermal treatment is lower.

2.4. Fuel cell preparation

Platinum wires were attached to the electrode surfaces of the fuel cells for current collection using different ink compositions. So, Ni + CGO 10% by weight inks were prepared from commercial nickel powders of 99.9% purity and 2.2–3.0 μm average grain size, dispersed in a resin. Cathode contacts were performed with the same ink that was used for cathode film deposition. So, both surfaces of the fuel cells were painted with prepared inks of Ni + CGO 10% by weight for the anode and LSCO + CGO 10% by weight for the cathode. An additional thermocouple was placed in direct contact with the centre of the anode surface in order to determine the real temperature of the fuel cells. The fuel cells so fabricated were placed in a quartz tube reactor of 23 mm of internal diameter, where a mixture of N₂ + O₂ with the air composition (80:20%, respectively) was circulated at different flux rates from 200 to 450 cm³ min⁻¹. The influence of propane flux rate for electrochemical evaluation was analysed from 0 to 50 cm³ min⁻¹. Finally, the fuel cells were heated inside the quartz tube by a tubular furnace. It was found that the fuel cells were operating at actual temperatures of between 400 and 650 °C.

2.5. Electrical properties

The fuel cells prepared as described above were placed between two pairs of Pt wires attached by the Ni + CGO 10% ink for the anode and LSCO + CGO 10% for the cathode. Then, the device was introduced into a quartz tube placed in the centre of a tubular furnace and heated from room temperature in the same atmosphere that the cells have been measured. The organic part of the inks was eliminated during the heating at relatively low temperature. Electromotive forces (emfs) were measured using

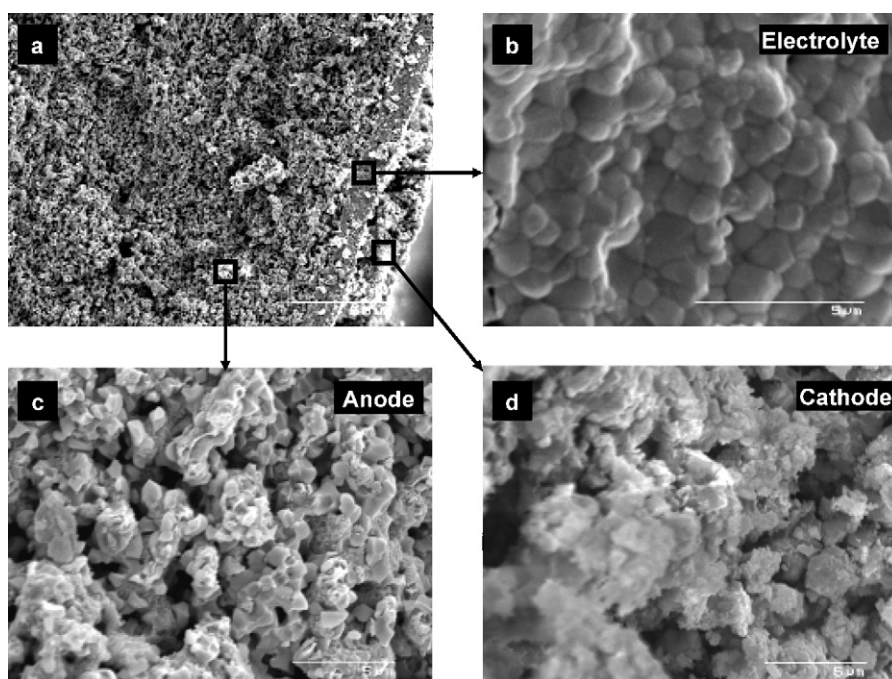


Fig. 3. SEM pictures of an anode-supported fuel cell with a 15 μm thick film of CGO. Anode-supported fuel cell (a) electrolyte (b) anode (c) cathode (d).

a Keithley 617 electrometer with an input resistance of $10^{14} \Omega$. The value of current was measured by reading the voltage drop in an auxiliary known resistance. I – V characteristics were determined by using the equipment for measuring current and voltage under variable loads. The temperature of the furnace was controlled by a temperature controller, and the temperature of the SOFC was measured using a Pt versus Pt-10% Rd thermocouple attached closely to the anode of the sample.

3. Results and discussion

We have found that the temperature of the fuel cells was approximately the same as that of the furnace at relatively low values, during heating. But, the temperature of the fuel cells is higher once the partial oxidation of propane takes place ($>350^\circ\text{C}$). Then, an electromotive force and an electrical current at $V \sim 0$ appears and the temperature of the fuel cells increases drastically. The actual temperature of the fuel cells was $\sim 100^\circ\text{C}$ higher than the furnace temperature during optimal operation of the fuel cells. Similar differences between the temperature of the fuel cells and the temperature of the furnace have been characterized and reported recently in the literature [18]. This difference in temperature increases at higher furnace temperatures, until the fuel cells operational temperature reaches $\sim 650^\circ\text{C}$, where the Open Circuit Voltage (O.C.V.) and the current density drop to zero. This deterioration of the electrical properties appears at fuel cell temperatures above 640°C , which corresponds to a furnace temperature of $\sim 550^\circ\text{C}$. So, the O.C.V. and the current density drop to zero at temperatures higher than 640°C , but the electrical properties could be recovered again by decreasing the temperature of the furnace. We have analysed the atmosphere

composition by chromatography and we have observed that the O_2 composition inside the quartz tube decreases drastically at this critical temperature. We have observed the same behaviour when we have substituted a fuel cell by an anode substrate in the same experimental conditions. So, the activity of the Ni in the anode substrate is very fast at these temperatures and the partial oxidation of the totality of the propane molecules take place. We have found an optimal ratio $\text{O}_2/\text{C}_3\text{H}_8 \sim 3$ in our experimental conditions but partial oxidation and total oxidation need a ratio of 1.5 and 5, respectively. So, the H_2 and CO_2 composition increases drastically but the O_2 composition decreases to zero and the fuel cells are deactivated due to the low oxygen partial pressure. On the hand, substantial reduction of Ce^{+4} to Ce^{+3} and decomposition of the LSCO do not take place at these temperatures and atmospheres. The fuel cells seem to be stable at fuel cell temperature lower than 640°C and show the same electrical characteristics after more than 3 h of reaction. The total resistance drops to a few $\text{k}\Omega$ at 300 – 320°C depending on the electrolyte thickness and the active surface of the cathode. Typical values of ~ 1 – $3 \text{ k}\Omega$ were found for a $20 \mu\text{m}$ thickness electrolyte and a surface of 10 mm^2 of painted LSCO + 10% CGO cathodes.

In another series of experiments, we explored the influence of the flux rate of the carrier gas (synthetic air) on the electrical properties and on the temperature of the fuel cells at a constant temperature of the furnace. Fig. 4 shows the current density and the temperature dependence of a fuel cell with a cathode active surface of 10 mm^2 annealed in the furnace at a constant temperature of 500°C , which corresponds to a fuel cell temperature of 585°C . Nevertheless, the O.C.V. is not very sensitive to the flux rate variation (see Fig. 5). The temperature of the fuel cell and the current density increase with the

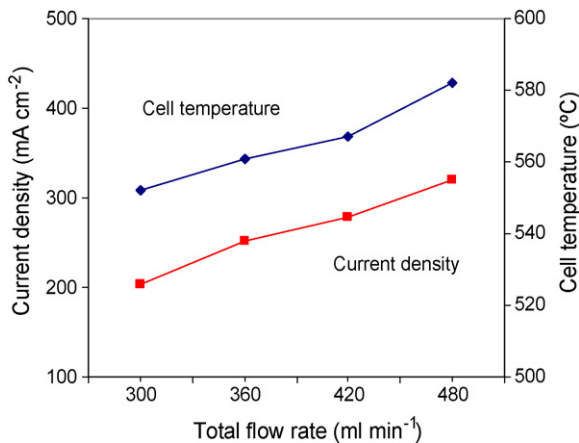


Fig. 4. Temperature and current density dependence vs. the total flux rate for an anode-supported fuel cell in a single-chamber reactor.

flux rate at a constant composition of the gases. So, stirring of the gases increases the partial oxidation of the propane and the temperature of the fuel cells. Probably, the partial oxidation reaction rate is limited by the elimination of some reaction products like CO_2 and H_2O through the porosity of the anode substrate. So, the reaction rate is activated when we increase the stirring of the gases or we reduce the thickness of the substrate.

The peak power density for a fuel cell operating at 585°C , which corresponds to a furnace temperature of 500°C , is represented in Fig. 6. In this figure we can see that the current density drops with voltage, but not linearly, and the peak of the power density is not symmetrical. Probably, this behaviour, which was not observed in electrolyte-supported fuel cells, is due to substrate effects. Effectively, electrolyte-supported fuel cells prepared with similar materials, and measured in the same operating conditions, do not show these effects [16]. On the hand, the O.C.V. is lower for the anode-supported fuel cells (0.7 V in front of 0.85 V for electrolyte-supported SOFCs) at similar temperatures. Probably, some defects in the film electrolyte produce

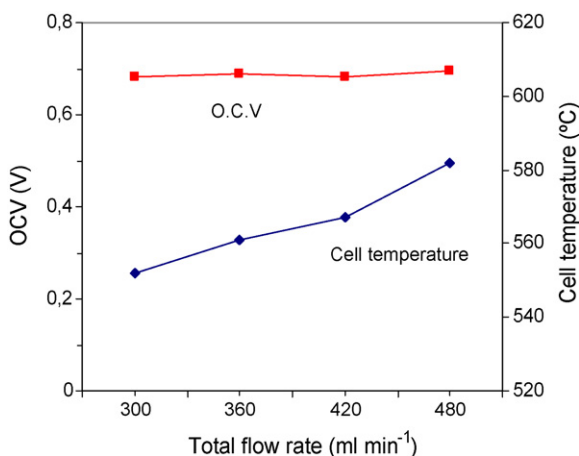


Fig. 5. Temperature and Open Circuit Voltage (O.C.V.) dependence vs. the total flux rate for an anode-supported fuel cell in a single-chamber reactor.

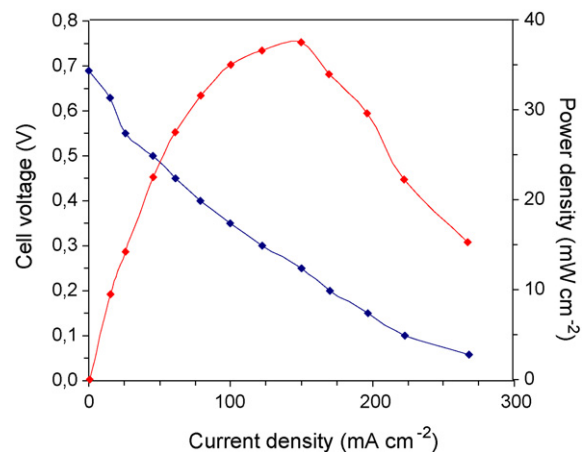


Fig. 6. Cell voltage and power density as function of current for a fuel cell of CGO supported-anode of Ni-CGO and LSCO-CGO as cathode measured at 585°C in a feed gas composition of 10 ml min^{-1} for propane and 450 ml min^{-1} for synthetic air.

this reduction in the O.C.V. Cracks and agglomerates have been found on the surface of some thick films prepared as described above (see Figs. 7 and 8). The electrical properties of the fuel cell with these types of defect decrease drastically due to small short circuits between the electrodes. Cracks are formed during densification at high temperature and depend on thermal treatments and rheological parameters of the inks such as viscosity, particle grain size, . . .etc. The Ni/CGO anode and the LSCO/CGO cathode seem to be stable under these experimental conditions. Nevertheless, more long term behaviour and cycling properties must to be undertaken in order to determine the veritable stability of the fuel cell.

Finally, we have investigated the O.C.V. and the current at $V \sim 0$ dependence with the flux of propane. We have found that there is only a narrow flux rate composition of propane where the electrical properties are optimal. A few ml min^{-1} lower or higher than the optimal propane flux rate decreases the O.C.V. and the current density of the fuel cells. This behaviour was very different in the electrolyte-supported fuel cells, where it was found that a critical propane partial pressure was necessary in order to start the reaction. Once the reaction was initiated, however, the O.C.V. and the current density variation with respect to propane partial pressure seemed to be zero or slightly negative [16]. Probably, this different behaviour was due to the quantity of Ni catalyst in the fuel cells. There was a very small quantity of Ni in the electrolyte-supported fuel cells compared to the anode-supported ones. So, the propane partial oxidation rate was higher in the anode-supported fuel cells at the same temperature. Finally, we have represented, in Fig. 9, the optimal flux rate of propane as a function of the total carrier gas flux rate. Optimal propane flux rate increases when we increase the total flux rate. This optimal ratio increases when we increase the total flux rate of the carrier gas. So, richest oxygen mixtures are needed at higher stirring rates. Further research in kinetics is necessary in order to understand the mechanisms involved in these types of fuel cell.

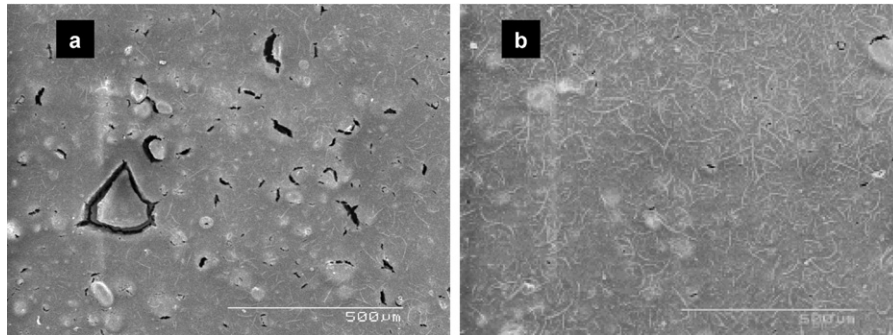


Fig. 7. Surface SEM pictures of two electrolytes with different density of defects. Cracks are formed during densification at high temperature.

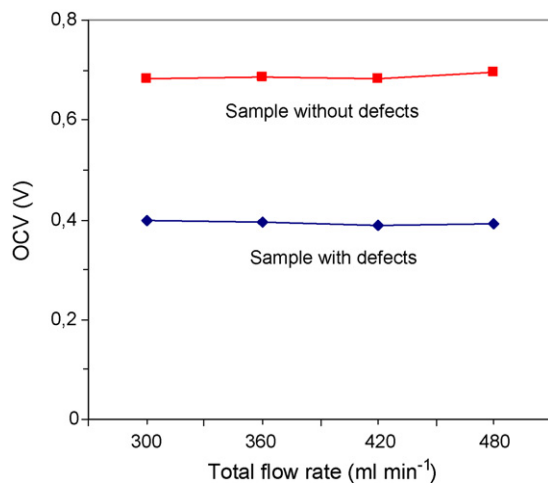


Fig. 8. Open Circuit Voltage (O.C.V.) for two anode-supported fuel cells prepared with CGO electrolytes. SEM picture shows cracks and agglomerates defects in the surface of some electrolytes.

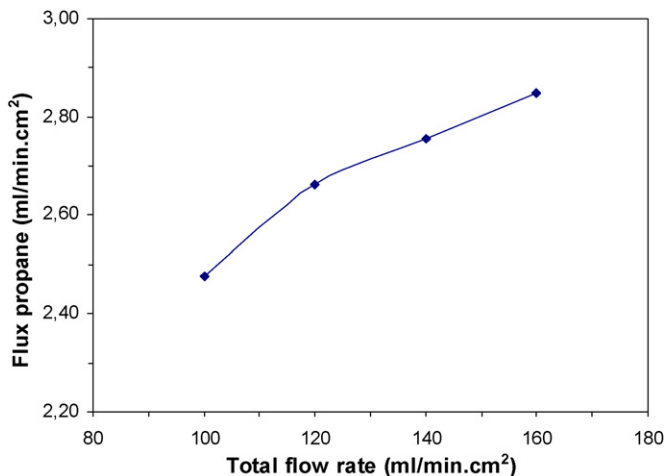


Fig. 9. Optimal flux rate of propane in function of the total flux rate for a furnace temperature of the 500 °C.

4. Conclusions

Anode-supported fuel cells working in single-chamber reactors are a promising alternative for the generation of high power densities, because it is possible to reduce considerably the thick-

ness of the electrolyte. Nevertheless, it is difficult to obtain good film quality of the electrolytes and an optimal porosity for the anode, at the same time. The $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ (LSCO) is a stable cathode in propane-diluted atmospheres for single-chamber solid oxide fuel cells based on anode-supported electrolytes, for working fuel cell temperatures as high as 640 °C. There is a considerable difference between the temperature of the furnace and the temperature of the fuel cells due to the exothermic propane partial oxidation on the anode. It is possible to increase the temperature difference between the furnace and the single-chamber fuel cells by increasing the insulation of the furnace. So, the heating produced by the partial oxidation of propane could be used to help to maintain the fuel cell operational conditions. Electrical properties of the fuel cells depend strongly on the atmosphere composition and flux rates of the total carrier gases, but the optimization of parameters is possible in order to obtain good power and current densities. So, single-chamber anode-supported fuel cells are a promising alternative for the fabrication of low temperature solid oxide fuel cells operating between 500–640 °C in propane-diluted atmospheres.

Acknowledgements

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